

**Sludge from paper mill effluent treatment as raw material to produce  
carbon adsorbents: an alternative waste management strategy**

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## Abstract

Pulp and paper industry produces massive amounts of sludge from wastewater treatment, which constitute an enormous environmental challenge. A possible management option is the conversion of sludge into carbon-based adsorbents to be applied in water remediation. For such utilization it is important to investigate if sludge is a consistent raw material originating reproducible final materials (either over time or from different manufacturing processes), which is the main goal of this work. For that purpose, different primary (PS) and biological sludge (BS) batches from two factories with different operation modes were sampled and subjected to pyrolysis (P materials) and to pyrolysis followed by acid washing (PW materials). All the materials were characterized by proximate analysis, total organic carbon (TOC) and inorganic carbon (IC), Fourier transform infrared spectroscopy (FTIR) and specific surface area ( $S_{\text{BET}}$ ). Sludge from the two factories proved to have distinct physico-chemical properties, mainly in what concerns IC. After pyrolysis, the washing step was essential to reduce IC and to considerably increase  $S_{\text{BET}}$ , yet with high impact in the final production yield. Among the materials here produced, PW materials from PS were those having the highest  $S_{\text{BET}}$  values (387-488 m<sup>2</sup> g<sup>-1</sup>). Overall, it was found that precursors from different factories might originate final materials with distinct characteristics being essential to take into account this source of variability when considering paper mill sludge as a raw material. Nevertheless, for PS, low variability was found between batches, which points out to the reliability of such residues to be used as precursors of carbon adsorbents.

**Keywords:** Waste valorization; Circular Economy; Alternative adsorbents; Carbon materials; Environment; Pyrolysis

## 1. Introduction

Pulp and paper industry is considered to be one of the most important industrial segments in the world. The enormous water requirements of this industry results in the generation of huge volumes of wastewater (on average, in a typical paper mill, between 1.5 and 60 m<sup>3</sup> of effluent is generated for each ton of paper) (Adhikari and Bhattacharyya, 2015; Soucy et al., 2014). As a consequence of the effluent treatment, a large quantity of sludge is produced, which represents a massive environmental burden. Biological (BS) and primary sludge (PS) are amongst the produced solid wastes and their properties depend on the manufacturing process, namely wood preparation, pulp and paper manufacture, chemical recovery, recycled paper processing and wastewater treatment (Buruberri et al., 2015; Monte et al., 2009; Pervaiz and Sain, 2015; Vochozka et al., 2016). On average, a total of 40 to 50 kg of dry sludge is produced for each ton of paper, 70% of which is PS and 30% is BS (Bajpai, 2015).

In recent years, and considering that environmental legislation is increasingly stringent, the pulp and paper industry has been facing some challenges with respect to the management of the resulting wastes. This aspect has to be linked to economic aspects in order to apply feasible solutions for waste management/valorization (Buruberri et al., 2015; Kamali and Khodaparast, 2015; Pervaiz and Sain, 2015). In the case of sludge from wastewater treatment, management options include incineration (approximately 19% of sludge is incinerated on-site) for energy recovery, land application to enhance soil fertility on agricultural and forest areas and production of ethanol (Bajpai, 2015; Likon and Trebše, 2012; Pervaiz and Sain, 2015). However, the most common practice has always been the landfill disposal of sludge (Likon and Trebše, 2012; Pervaiz and Sain, 2015). Landfills can be owned and operated by the industry itself or can be independently maintained, requiring a payment from the mills. In any case, landfills should comply with the requirements of the European Landfill Directive (1999/31/EC) (Likon and Trebše, 2012). Nevertheless, landfilling is not recommended and is being discouraged since it causes environmental problems related with leaching and greenhouse gas production (Reckamp et al., 2014). The Confederation of European Paper Industries (CEPI) supports a complete ban of landfilling and incineration in the European Union in agreement

with the Waste Framework Directive (2008/98/EC) which lays down some basic waste management principles, prioritizing recycling over energy recovery and disposal. Also, the European Commission Roadmap to a Resource Efficient Europe (COM (2011) 571) foresees the sustainability of the Europe's economy by 2050, proposing milestones to be reached by 2020 in which waste will be managed as a resource and energy recovery will be limited to non-recyclable materials (CEPI, 2016; European Commission, 2016a, 2016b). Therefore, sustainable practices must be developed, involving the valorization of wastes, by using them as raw materials for distinct purposes (Buruberri et al., 2015). In this context, some innovative approaches for the conversion of sludge from the paper industry into new materials have been explored in the past two decades. Promising innovations include the use of such sludge as heat insulation material, paper and wood adhesive, dried mixture for use as pesticides or fertilizers carriers in agriculture and as building material (Buruberri et al., 2015; Likon and Trebše, 2012; Pervaiz and Sain, 2015). Also, given the carbonaceous nature of paper mill sludge, their conversion into activated carbon with application on water remediation has been proposed by several authors (*e.g.* Devi and Saroha, 2014; Ferreira et al., 2016a; Khalili et al., 2000; Khalili et al., 2002; Pirzadeh and Ghoreyshi, 2014; Reckamp et al., 2014). This conversion, besides reducing the environmental problems associated with the disposal of wastes, also enhances wastewater treatment by using materials from industrial waste itself, and helps the preservation of naturally-existing resources usually applied in the production of activated carbons (Khalili et al., 2002). Adsorbents originated from paper mill sludge have already been applied in the adsorption of phenolic compounds (Devi and Saroha, 2014; Devi and Saroha, 2015; Masomi et al., 2015; Pirzadeh and Ghoreyshi, 2014), dyes (Auta and Hameed, 2014; Li et al., 2011), heavy metals (Battaglia et al., 2003) or pharmaceuticals (Calisto et al., 2014; Calisto et al., 2015; Ferreira et al., 2015; Ferreira et al., 2016b; Jaria et al., 2015) from contaminated waters.

There is a relationship between the properties of an adsorbent material and its effectiveness (*i.e.* enhanced adsorption capacity), these characteristics being importantly determined by the used precursor and the production process (Gonzalez et al., 1995; Namazi et al., 2010). Therefore, in order to evaluate the appropriateness of pulp and paper mill sludge as

precursor for the production of carbon adsorbents, it is essential to know if these wastes are a consistent and reliable raw material, guaranteeing the repeatability of the final product through time. However, no attention is given to this aspect when studying the production of alternative adsorbents from pulp and paper mill sludge (and other residues in general) – as far as authors know, there are no studies concerning this subject.

This work aimed to assess, for the very first time, the consistency of carbon adsorbents produced by the pyrolysis of sludge from the paper industry. With this purpose, four PS and BS batches collected from two factories with different operation characteristics were used in this work. Moreover, in order to conclude about the potential of the obtained materials as adsorbents, key physicochemical properties were determined and the influence of the raw materials on these properties evaluated. All the materials (raw sludge and resulting carbons) were characterized by proximate analysis, N<sub>2</sub> adsorption isotherms (specific surface area ( $S_{BET}$ ) and porosity determination), total organic carbon (TOC) and inorganic carbon (IC) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR).

## 2. Experimental section

### 2.1. Factory description and sludge production

Sludge from two paper industries, hereafter named Factory 1 (F1) and Factory 2 (F2), were used in this work. Both factories use a kraft elemental chlorine free (ECD) pulp production process and operate using *Eucalyptus globulus* wood. Factory 1 has more than 6 decades of existence and was the first one, worldwide, to produce paper pulp from eucalyptus wood by the kraft process. Its production reaches about 320,000 tons of bleached pulp per year, while the Factory 2 production reaches approximately 570,000 tons of bleached eucalyptus kraft pulp and 800,000 tons of uncoated woodfree (UWF) printing paper. Therefore, Factory 2 combines the production of pulp and paper, while Factory 1 produces only pulp.

On average, in both factories, PS and BS are produced at a rate of 20 and 10 kg per ton of air dried pulp, respectively. These solid wastes are generated during the effluent treatment. PS results from fibers rejected after the cooking/digestion of the pulp and losses of fibers and

1 other solids which occur when liquid effluents are involved (for example, washing and  
2 bleaching). The composition of PS is very similar to the pulp, consisting essentially of organic  
3 matter (mostly composed of fibrous materials) (Calisto et al., 2014; Soucy et al., 2014). After  
4 primary treatment, the remaining suspended solids are then submitted to bacterial digestion,  
5 under aerobic conditions, which generates BS. Some studies indicate that this type of sludge  
6 may have lignin in its composition and no cellulose or hemicelluloses; therefore, BS is  
7 considered to be constituted mostly by biomass (after dehydration) (Calisto et al., 2014; Soucy  
8 et al., 2014). This process generates a large amount of sludge due to the microbial growth.  
9 However, the generated volume of BS is lower than that of PS since most of the heavy, fibrous  
10 and/or inorganic solids are removed during the primary treatment (Monte et al., 2009).  
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## 24 *2.2. Sludge collection and conditioning*

25 PS and BS were collected four times from each F1 and F2 in campaigns separated by 15  
26 days from each other. After collection, PS and BS were firstly dried at room temperature,  
27 followed by a 24 h period at 105 °C in an oven. BS was grinded with a mortar grinder and  
28 sieved (the 0.5-1.0 mm fraction was used in this work). In the case of PS, a blade mill was used  
29 after drying, resulting in an extremely light net of fibrous material that was not possible to sieve.  
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38 Sludge samples are referred as F1PS1, F1PS2, F1PS3 and F1PS4, for the four PS  
39 batches from Factory 1 (F1PS); F2PS1, F2PS2, F2PS3 and F2PS4, for the four PS batches from  
40 Factory 2 (F2PS). An equivalent nomenclature was defined for BS samples, using, for example,  
41 F1BS1 for the first batch of BS from Factory 1.  
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## 49 *2.3. Carbon adsorbents production*

### 50 *2.3.1 Pyrolysis*

51 After sludge collection and conditioning, PS and BS samples were separately pyrolysed  
52 into porcelain crucibles in a muffle (Nüve, series MF 106, Turkey). The pyrolysis was carried  
53 out under inert atmosphere (nitrogen flow), at 800 °C for 150 min (heating rate of 10 °C min<sup>-1</sup>).  
54 Detailed information concerning the pyrolysis process and the selection of the production  
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conditions can be found in a previous work (Calisto et al., 2014). Pyrolysed materials (P materials) are referred by adding “P” to the nomenclature used for the respective raw material (as defined in section 2.2) using, for example, F1PS1-P.

### 2.3.2 Washing

After pyrolysis, carbons were washed with 1.2 M HCl followed by distilled water until the washing solution reached neutral pH. The purpose of this washing procedure was to remove ashes and other inorganic matter, in order to improve microporosity and surface area by unblocking obstructed pores. Finally, the produced carbons were dried in an oven at 105 °C for 24 h. When referring materials subjected to washing after pyrolysis (PW materials), “PW” is added to the terminology of the respective raw material (as defined in section 2.2) using, for example, F1PS1-PW.

## 2.4 Characterization of raw materials and carbon adsorbents

### 2.4.1 Total organic carbon (TOC) and inorganic carbon (IC)

Total carbon (TC) and inorganic carbon (IC) analyses were performed using a TOC analyzer (Shimadzu, model TOC-V<sub>CPH</sub>, SSM-5000A, Japan) on the raw materials (PS and BS) and the produced carbon adsorbents. All the materials were analyzed in triplicate. TOC was calculated by difference between TC and IC.

### 2.4.2 Fourier transform infrared spectroscopy (FTIR)

The attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) spectra were obtained by a Shimadzu-IRaffinity-1 equipment, using an ATR module, under a nitrogen purge. The measurements were recorded in the range 600–4000 cm<sup>-1</sup>, 4.0 of resolution, 128 scans and with atmosphere and background correction. ATR-FTIR was measured on the raw materials (PS and BS) and all the P and PW materials produced from them.

### 2.4.3 Nitrogen adsorption isotherms

Aiming the physical characterization of all the P and PW materials here produced, the specific surface area ( $S_{\text{BET}}$ ) and micropore volume ( $W_0$ ) were determined by nitrogen adsorption isotherms. No  $S_{\text{BET}}$  determination was carried out for PS and BS since they are non-microporous materials (Calisto et al., 2014).

These isotherms were acquired at 77 K using a Micromeritics Instrument, Gemini VII 2380 after outgassing the materials overnight at 120 °C.  $S_{\text{BET}}$  was calculated from the Brunauer–Emmett–Teller equation (Brunauer et al., 1938) in the relative pressure range 0.01–0.1. Pore volume ( $V_p$ ) was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.99.  $W_0$  was determined by applying the Dubinin–Radushkevich equation (Dubinin, 1966) to the lower relative pressure zone of the nitrogen adsorption isotherm.

#### 2.4.4 Proximate analysis

Proximate analysis was performed by thermogravimetric analysis (TGA) on the raw materials and all the PW materials produced from them. P materials were not analyzed since it was concluded by the  $S_{\text{BET}}$  determination that they do not present attractive surface areas and micropore volumes and therefore would not present adsorptive potential (see section 3.1.3). The analysis was carried out in a thermogravimetric balance Setsys Evolution 1750, Setaram, TGA mode (S type sensor). Standard methods to determine the moisture (UNE 32002) (AENOR, 1995), volatile matter (UNE 32019) (AENOR, 1985) and ash content (UNE 32004) (AENOR, 1984) were employed. The experimental procedure for TGA consisted of the sample heating, under nitrogen atmosphere, from room temperature to 105 °C (heating rate of 10 °C min<sup>-1</sup>); sample was kept at this temperature until total stabilization of the sample mass (approximately 30 min); next, temperature was increased from 105 to 950 °C (10 °C min<sup>-1</sup>), keeping the sample at 950 °C until total stabilization of the sample mass (approximately 30 min); finally, at 950 °C, the carrier gas was automatically switched to air and the sample was maintained at 950 °C until total stabilization of the sample mass. The mass loss observed around 105 °C is attributed to moisture; the mass loss registered from the end of this first step up to the switching of the carrier gas corresponds to volatile matter; the mass loss comprised between the introduction of



the air flow and the stabilization of the mass is attributed to fixed carbon content; and lastly the final residue (stabilized mass) corresponds to ash content.

## 2.5 Variability of the carbon adsorbents production process

In order to guarantee that the observed variability between factories and batches is not due to the carbon production process (pyrolysis and acid washing), it is important to assure the consistency of those procedures. The repeatability of the pyrolysis process was evaluated by performing replicates of the pyrolysis for the first batch of PS from Factory 1 (F1PS1-P). Moreover, due to the major influence of the acid washing in the characteristics of the final material, this step was also evaluated. Both the effect of the washing time (60 and 300 min) and the repeatability of the washing process were assessed by performing 3 replicates of each washing time for materials produced from the first batch of PS and BS from Factory 1 (F1PS1-PW and F1BS1-PW). All the resulting materials were analyzed by IC, TOC and  $S_{\text{BET}}$ .

## 3. Results and Discussion

### 3.1 Characterization of raw materials and carbon adsorbents

#### 3.1.1 Total organic carbon (TOC) and inorganic carbon (IC)

The TOC and IC results (Fig. 1; Table S1 in Supporting Material (SM)) revealed that the raw materials from Factory 1, for both PB and BS, presented higher levels of IC than those from Factory 2 and TOC was significantly lower for the raw materials from Factory 1 than from Factory 2. Overall, the pyrolysis process resulted in a decrease of TOC, except for BS from Factory 2, which TOC increased after pyrolysis. After the HCl washing step of the P materials, a significant increase in the percentage of TOC was verified while the IC fell to negligible values, showing that the acid washing was effective in the removal of the inorganic carbon. Further changes due to the washing procedure will be evaluated in the subsequent sections.

Considering the consistency of the materials, the highest variability between sludge batches was observed for the TOC contents of raw materials from Factory 1 (relative standard deviation

(RSD) for PS and BS of 36 and 32%, respectively) and for pyrolysed PS from Factory 1 (RSD of 44%). These three described cases of high variability are characterized by a high content in IC. The highest RSD are a consequence of the relatively low values of TOC (for the raw materials from Factory 1) and do not reflect meaningful fluctuations in the values of this parameter. Lower variability (RSD in the range 3-14%) was observed for all the other batches (raw materials, P and PW materials from Factory 2 and PW materials from Factory 1).

### 3.1.2 ATR-FTIR

The ATR-FTIR spectra obtained for PS, BS and the carbon adsorbents (P and PW materials) obtained from them are depicted in SM (Fig. S1 and S2). Considering that spectra of different batches of the same material did not present noticeable differences, only one batch is exemplified in Fig. 2 (the first batch of PS and BS and resulting carbons for both factories).

The results (Fig. 2 and Figs. S1 and S2) show that the precursor materials (both PS and BS) have a much more complex chemical composition than the P materials and even more than the PW materials.

In the case of raw PS (Fig. S1) from both factories, the FTIR spectra evidenced the presence of two main peaks at  $\sim 1400$  and  $\sim 850$   $\text{cm}^{-1}$  which, in conjugation, point out to the presence of carbonates. The relative intensity of these peaks (when compared with other peaks/bands of the spectra) is higher for raw materials from Factory 1 than from Factory 2, which indicates that the first presented a higher content in inorganic matter. This fact can be easily confirmed by IC results (Fig. 1; Table S1). In these spectra (Fig. S1), one can also identify broad bands between 3200 and 3600  $\text{cm}^{-1}$ , attributed to O-H stretching from hydroxyl groups of cellulose and water (Calisto et al., 2014). This can be observed in almost all the batches from both factories, although in the raw materials from Factory 1 this band is not so evident maybe due to the high intensity of the carbonate peaks. In the *fingerprint* region, several peaks are present between 1650 and 1150  $\text{cm}^{-1}$ . These peaks can be associated, for instance, to C–O–C stretching vibration of pyranose ring ( $\sim 1150$   $\text{cm}^{-1}$ ) and to C–H bending vibrations ( $\sim 1300$   $\text{cm}^{-1}$ ) (Calisto et al., 2014; Jaria et al., 2015). In both Factory 1 and Factory 2, several

peaks/bands around 1200 and 1000  $\text{cm}^{-1}$  can be observed and can be related to alcohol groups (around 1050  $\text{cm}^{-1}$  it corresponds to primary alcohols C-O stretch; around 1100  $\text{cm}^{-1}$  it corresponds to secondary alcohols C-O stretch; around 1150  $\text{cm}^{-1}$  to tertiary alcohols C-O stretch, and around 1200  $\text{cm}^{-1}$  to phenol C-O stretch) (Coates, 2000). Also, peaks in the ranges 1150-1050  $\text{cm}^{-1}$  and 1140-1070  $\text{cm}^{-1}$  might be derived from the presence of alkyl-substituted ether and cyclic ethers (large rings (C-O-C stretch)), respectively (Coates, 2000). The peak around 1650  $\text{cm}^{-1}$  is associated to carbonyl groups (Calisto et al., 2014; Coates, 2000); the peaks in the range 750-450  $\text{cm}^{-1}$  correspond to in-plane and out-plane aromatic ring deformation vibrations, C-H and C-C stretching (Jaria et al., 2015). Overall, the spectra obtained for PS are similar to the cellulose spectrum (Méndez et al., 2009).

Regarding BS (Fig. S2), the spectra obtained for raw materials from Factory 1 are similar to those obtained for PS (Fig. S1) from the same factory. However, the spectra determined for BS from the two factories are very different. Once again, there is a high relative intensity of the peaks related to carbonates, which may difficult the identification of other characteristic peaks. Relatively to BS from Factory 2, the occurrence of several peaks identified for PS, namely, the broad band between 3100 and 3600  $\text{cm}^{-1}$  and weak and medium absorption peaks/bands in the range 1670-1620  $\text{cm}^{-1}$ , can be observed. Other bands such as the ones around 1000, 1200 and 1500  $\text{cm}^{-1}$  are indicative of the presence of aromatic groups and absorption at ~1200  $\text{cm}^{-1}$  can be attributed to phenol C-O stretch or to aryl-O stretch in aromatic ethers (Calisto et al., 2014; Coates, 2000). In the spectra of these raw materials (BS from Factory 2; Fig. S2) the peaks related to the carbonate groups (~1400 and 850  $\text{cm}^{-1}$ ) appear to be absent. The overall spectra are very similar to that of lignin (Beyer et al., 1997; Calisto et al., 2014).

In the case of P materials (Figs. S1 and S2), the presence of carbonate ions continues to be evident. For pyrolysed PS (Fig. S1), it can be observed that these peaks appeared almost in all cases, but are more pronounced in the case of Factory 1; for pyrolysed BS (Fig. S2), only those from Factory 1 present this combination of characteristic peaks. The washing of the P materials resulted in the disappearance of the majority of the bands (implying the absence of the main functional groups identified in the raw materials) and, in general, there was a low variability in

the ATR-FTIR spectra between batches and between factories, for all the materials produced from both PS and BS. The most evident inference is the disappearance of the peaks related to the presence of carbonates. Moreover, a peak in the region 1615-1495 cm<sup>-1</sup> was observed, indicating the presence of aromatics. A peak around 1300 cm<sup>-1</sup> was also identified and can be associated to different groups, including carboxylic acids or aryl-amines (Pavia et al., 2001), or to the alcohols O–H stretch or to aromatic ring stretches (Calisto et al., 2014).

Overall, it can be said that using ATR-FTIR no significant differences are observed between batches.

### 3.1.3 Specific surface area ( $S_{\text{BET}}$ )

The  $S_{\text{BET}}$  determined for the carbon adsorbents herein produced are shown in Fig. 3 and in SM (Table S2). From the displayed results it is clear that the acid washing resulted in a remarkable increase of the  $S_{\text{BET}}$  of P materials. Overall, this increase was also observed for  $W_o$  (Table S2) - traditionally regarded as a key factor for optimum removal efficiencies in carbon adsorbents (Cabrita et al., 2010). These results point to acid washing as an essential step for unblocking occluded pores after the pyrolysis of PS and BS and, therefore, for the production of carbon adsorbents from them. In any case, quite low  $S_{\text{BET}}$  values were determined for BS-PW from Factory 2 as compared with the other PW materials. It can also be observed that materials from Factory 1 (either PS or BS) presented higher  $S_{\text{BET}}$  than materials from Factory 2. The largest  $S_{\text{BET}}$  values determined ( $424 \pm 45 \text{ m}^2 \text{ g}^{-1}$ ) were those of the PS-PW.

In general, BS-PW presented higher variability between batches (RSD of 37% and 58% for Factory 1 and 2, respectively) in comparison with the corresponding materials obtained from PS (RSD of 11 and 16% for Factory 1 and 2, respectively). This higher variability may be related to the larger heterogeneity of the raw material, since the generation of BS includes the bacterial digestion of the organic content of the sludge. Then, PS-PW from both factories not only presented consistent  $S_{\text{BET}}$  values but also relative high  $S_{\text{BET}}$ , which are key features for the production of carbon adsorbents.

### 3.1.4 Proximate Analysis

Proximate analysis results are depicted in Fig. 4 and Table S3. For the raw materials, the ash content of Factory 1 is much higher compared to that of Factory 2 (approximately twice the value, in the case of PS, and thrice the value in the case of BS). These results are in accordance with those from TOC (Fig. 1 and Table S1) and ATR-FTIR spectra (Figs. 2, S1 and S2). Also, Factory 1 has, in general and for both PS and BS, lower values of fixed carbon and volatile matter than Factory 2. Considering the described variations, the factories presented a distinct profile in what concerns proximate analysis.

Concerning the effects of pyrolysis and washing, PW materials registered a considerable increase in the fixed carbon and a decrease in the volatile matter. This tendency was observed for PW materials obtained from both PS and BS of the two factories. Despite the verified differences between factories for the raw materials, the resulting PW materials presented a similar pattern indicating that the variability in the proximate analysis profile of the precursors did not imply PW materials with distinct characteristics. The ash content of the PW materials was in line with these conclusions: while, as previously referred, raw materials from Factory 1 had two to three times the ash content of the Factory 2, the ash content of PW materials was similar for both factories.

## 3.2 Production of adsorbent materials from paper mill sludge: practical implications

### 3.2.1 Variability of the carbon adsorbents production process

The evaluation of the repeatability of the pyrolysis process revealed no major differences with values ranging from  $10.4 \pm 0.3$  to  $11.7 \pm 0.4\%$  for IC,  $1.8 \pm 0.3$  to  $1.7 \pm 0.2\%$  for TOC and  $1.36 \pm 0.02$  to  $4.2 \pm 0.4 \text{ m}^2 \text{ g}^{-1}$  for  $S_{\text{BET}}$ . Concerning possible variations due to the acid washing, washing times of 60 and 300 min were both found to produce reproducible materials in what concerns  $S_{\text{BET}}$  ( $S_{\text{BET}} \text{ RSD}_{60 \text{ min}} = 0.75\%$  and  $S_{\text{BET}} \text{ RSD}_{300 \text{ min}} = 0.56\%$ ;  $n = 3$ ). Also, it was found that the longer washing time (300 min) had no advantages in obtaining a higher  $S_{\text{BET}}$  ( $S_{\text{BET } 60 \text{ min}} = 480 \pm 4 \text{ m}^2 \text{ g}^{-1}$  and  $S_{\text{BET } 300 \text{ min}} = 443 \pm 2 \text{ m}^2 \text{ g}^{-1}$ ). The same conclusions were obtained by IC and TOC determination ( $\text{IC}_{60 \text{ min}} = 0.088 \pm 0.001\%$  and  $\text{IC}_{300 \text{ min}} = 0.040 \pm 0.005\%$ ;  $\text{TOC}_{60 \text{ min}} =$

52 ± 1% and TOC<sub>300 min</sub> = 54 ± 2%). Therefore, the washing time of 60 min was the one chosen and used in the further studies.

Overall, these results confirm that the pyrolysis and washing (including washing time) are not a relevant source of variability in the production of the carbon adsorbents from paper industry sludge.

### 3.2.2 Impact of the raw materials characteristics in the production of carbon adsorbents

Obtaining final materials with interesting physico-chemical characteristics (high  $S_{\text{BET}}$ , high TOC and low ash content) is a key step for considering the valorization of paper mill sludge for the production of carbon adsorbents. However, the feasibility of such application should also be evaluated considering the consistency of the produced materials over time and it is also crucial to be aware if factories with different production processes result in carbon materials with distinct properties. Only with the evaluation of such variability one can conclude about the reliability of the produced materials for large scale and/or continuous production and application.

The results here described show that sludge collected from Factory 1 has very high IC contents (Fig. 1; Table S1), most certainly calcium carbonate used as a blanching agent in the pulp and paper manufacturing. This fact is evidenced by ATR-FTIR spectra (which present peaks/bands typical of carbonates; Figs. 2, S1 and S2), IC determination (Fig. 1; Table S1) and proximate analyses (Fig. 4; Table S3). A high IC content is generally not desirable for raw materials intended for the production of carbon adsorbents. In fact, after pyrolysis, sludge from Factory 1 continues to have a relative large IC content (Fig. 1; Table S1), which was effectively reduced by the subsequent acid washing. However, in the case of sludge from Factory 1, despite the effectiveness of the washing step in the reduction of IC, increase of TOC and high improvement of the  $S_{\text{BET}}$  (Fig. 3; Table S2), the final yield of production (pyrolysis and washing) of the corresponding carbon material is very low (around 4 and 13% for PS and BS, respectively). On the other hand, both PS and BS from Factory 2 have very low IC content with

1 direct impact in the global yield of production (around 10 and 35% for PS and BS,  
2 respectively). The high IC content also had consequences in the hardness and resistance of the  
3 produced materials. Carbons derived from PS, from both factories, are necessarily powdered  
4 carbons, considering that PS is fibrous in nature. Yet, in the case of BS from Factory 1, it was,  
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6 in fact, possible to obtain granular carbons by pyrolysis but grains did not resist to the acid  
7 washing. Contrarily, BS from Factory 2, which had a low IC content, was appropriate for the  
8 production of a granular adsorbent that was resistant to the acid washing. Overall, the high IC  
9 content of raw materials resulted in two major drawbacks: *a)* low production yields and *b)*  
10 reduced hardness/strength of the materials to withstand use as granular carbon adsorbents.  
11 Nevertheless, the presence of carbonates might also have positive implications in the specific  
12 surface areas. Sludge from Factory 2, with low IC (particularly in the case of BS), consistently  
13 resulted in carbon materials with lower  $S_{\text{BET}}$  values. Considering that alkali metal carbonates are  
14 used as activating agents for inducing the development of microporosity and surface area  
15 (Viswanathan et al., 2009), the carbonates naturally present in the sludge from Factory 1 might  
16 have triggered some kind of chemical activation process. In any case, the high  $S_{\text{BET}}$  values here  
17 obtained for materials produced by the pyrolysis and acid washing of PS from both factories,  
18 together with the uniformity between batches, point to the possible applicability of these carbon  
19 adsorbents for wastewater treatment. These findings are encouraging for further investigation  
20 concerning the improvement of such properties, namely through activation procedures.  
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### 44 *3.2.3 Considerations on the large-scale applicability of the paper mill sludge* 45 46 *pyrolysis*

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48 Regarding the production of the adsorbent materials here studied, it must be highlighted  
49 that pyrolysis, also called carbonization or destructive distillation, is a thermochemical  
50 conversion option that may be used for the management of biowastes, constituting an alternative  
51 to incineration and landfill of sludge generated from wastewater treatment at the paper industry.  
52 Furthermore, pyrolysis of such sludge produces a mixture of gaseous and liquid (bio-oil) fuels,  
53 besides a solid inert residue (Bajpai, 2015), which, as it was shown in this study, presents  
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1 interesting physico-chemical properties that may lead to high adsorption capacity. On the  
2 whole, through the several obtained products, pyrolysis may allow for the recovery of 95-98%  
3 of the energy contained in dry sludge from the paper industry (Bajpai, 2015). Thus, the  
4 integration of the production of carbon adsorbents into a power generation plant might result in  
5 significant improvements in its economic feasibility due to the possibility of simultaneous  
6 energy recovery. Also, this work has shown consistent properties between different batches of  
7 both PS and BS within each factory; however, a lack of consistency was found between the two  
8 factories (which must be related to the different production processes). It was concluded that the  
9 verified differences between sludge from different factories had implications in the properties of  
10 the carbon adsorbents produced which might constitute an important drawback for the operation  
11 of centralized pyrolysis infrastructures. Moreover, centralization would mean large costs  
12 associated to the feedstock transportation. On the other hand, as shown by previous studies, the  
13 production costs might be significantly lowered by large production facilities due to competitive  
14 production cost related to the highest product output (Choy et al., 2005; Ng et al., 2003).  
15 Currently, large research is being done on new and sustainable systems for the pyrolysis of  
16 sludge from the paper industry. Yet, other processes should also be considered, such as, for  
17 instance, the use of microwave-assisted production as an alternative to pyrolysis which might  
18 significantly lower the energy requirements.

19  
20 Overall, after showing the adequacy of paper mill sludge as raw material for carbon  
21 adsorbents production, a complete economic analysis of the production and implementation  
22 costs should be performed, taking into consideration different process designs, in order to have  
23 an accurate assessment of the cost-effectiveness of such options.

#### 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65

**4. Conclusions**

The consistency of carbon adsorbents derived from the pyrolysis (followed or not by acid washing) of sludge generated from the treatment of effluents within the paper industry was here evaluated considering (i) the variability between different sludge batches, and (ii) the variability between two paper factories operating with different production processes. The



1 results showed that the major difference between raw materials from different factories was the  
2 IC content, which was much higher in the sludge from Factory 1 than in that from Factory 2.  
3 Yet, IC was effectively reduced by an acid washing step after pyrolysis, which also increased  
4 the corresponding TOC and considerably improved the  $S_{\text{BET}}$ . The high IC had important  
5 implications in the production yield and in the hardness of the produced materials (relative high  
6 IC meant lower production yields and lower materials' hardness). However, despite high IC  
7 content, higher  $S_{\text{BET}}$  were observed for both PS and BS materials from Factory 1, which  
8 presented very interesting properties in terms of surface area, especially considering that they  
9 were not subjected to a chemical activation. Still, considering  $S_{\text{BET}}$ , P and PW materials  
10 produced from BS presented relative high variability between batches, while the  $S_{\text{BET}}$  of  
11 materials from different batches of PS did not differ in more than 16%. Overall, it can be  
12 concluded that precursors from factories with different operation mode might originate final  
13 materials with distinct characteristics being therefore essential to take into account this source of  
14 variability when considering paper mill sludge as a raw material. On the other hand, low  
15 variability was found between materials produced from different batches of sludge for each  
16 factory, which is a good indicator of the reliability of such residues to be used as new resources.

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**Figure Captions**

**Fig. 1:** Inorganic carbon (IC, %) and total organic carbon (TOC, %) (obtained by difference between total carbon (TC, %) and IC) for raw, pyrolysed (P) and pyrolysed and washed (PW) materials (n = 3), for the four batches of both primary (PS) and biological sludge (BS) and both factories. Mean for each type of material is also shown.

**Fig. 2:** Examples of attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) spectra determined for the raw, pyrolysed (P) and pyrolysed and washed (PW) materials from the batch 1 for both primary (PS) and biological sludge (BS) and both factories.

**Fig. 3:** Specific surface area ( $S_{\text{BET}}$ ) for pyrolysed (P) and pyrolysed and washed (PW) materials produced from the four batches of both primary (PS) and biological sludge (BS) and both factories. Mean values for each type of material is also shown.

**Fig. 4:** Proximate analysis (wt%, dry basis) for raw and pyrolysed and washed (PW) materials. Presented values correspond to the mean for the four batches collected for each factory and type of sludge (MC – Moisture Content; A – Ash; VM – Volatile Matter; FC – Fixed Carbon).

Figure 1  
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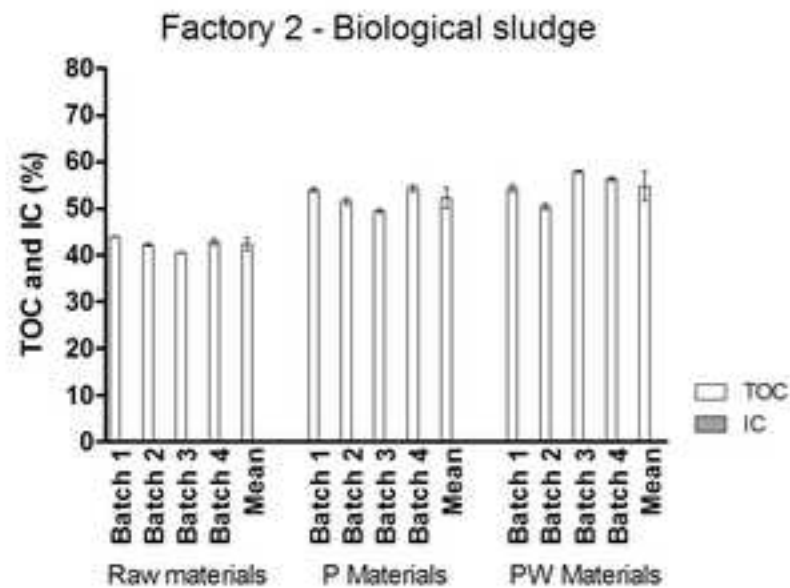
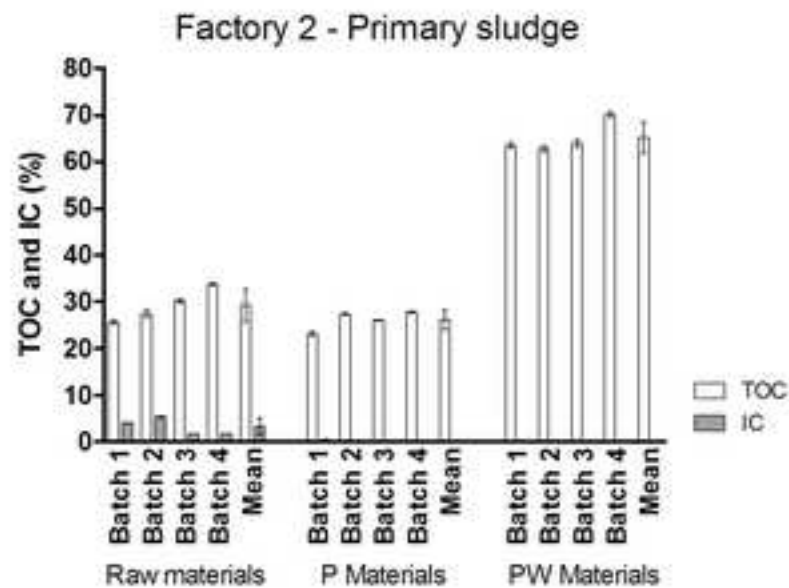
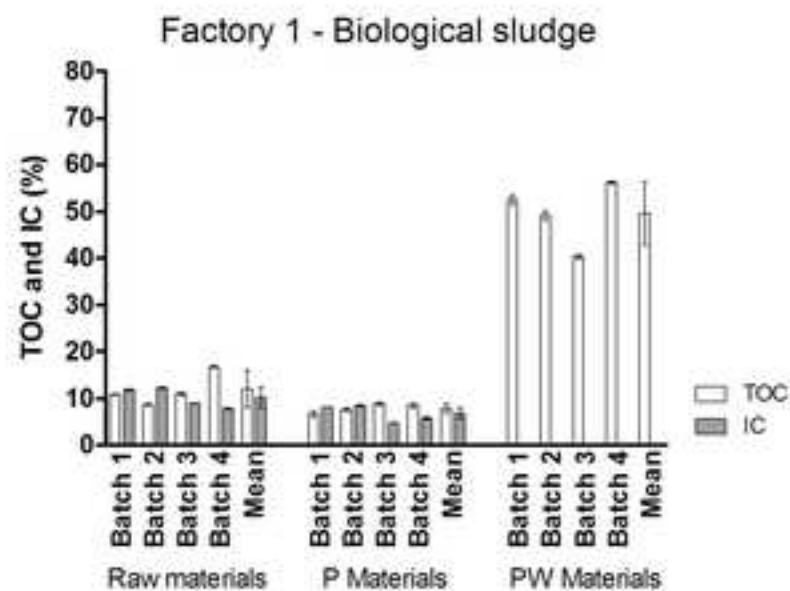
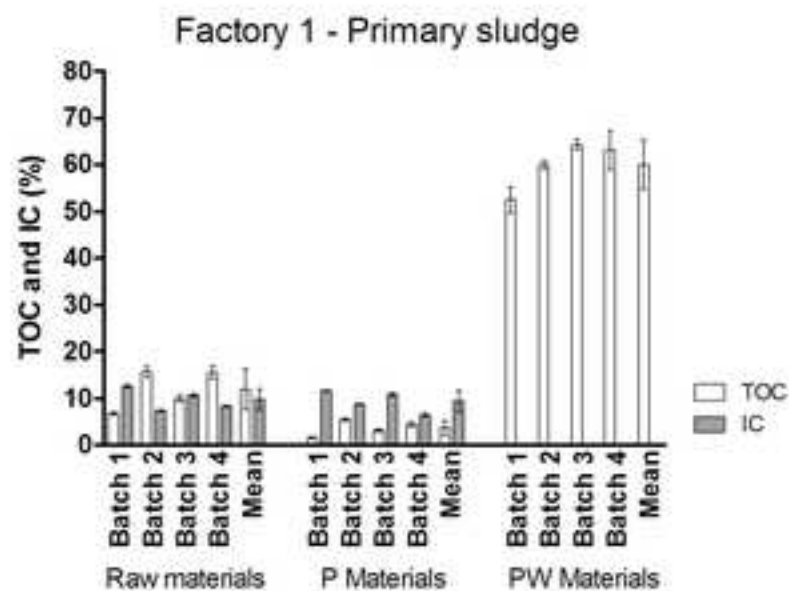


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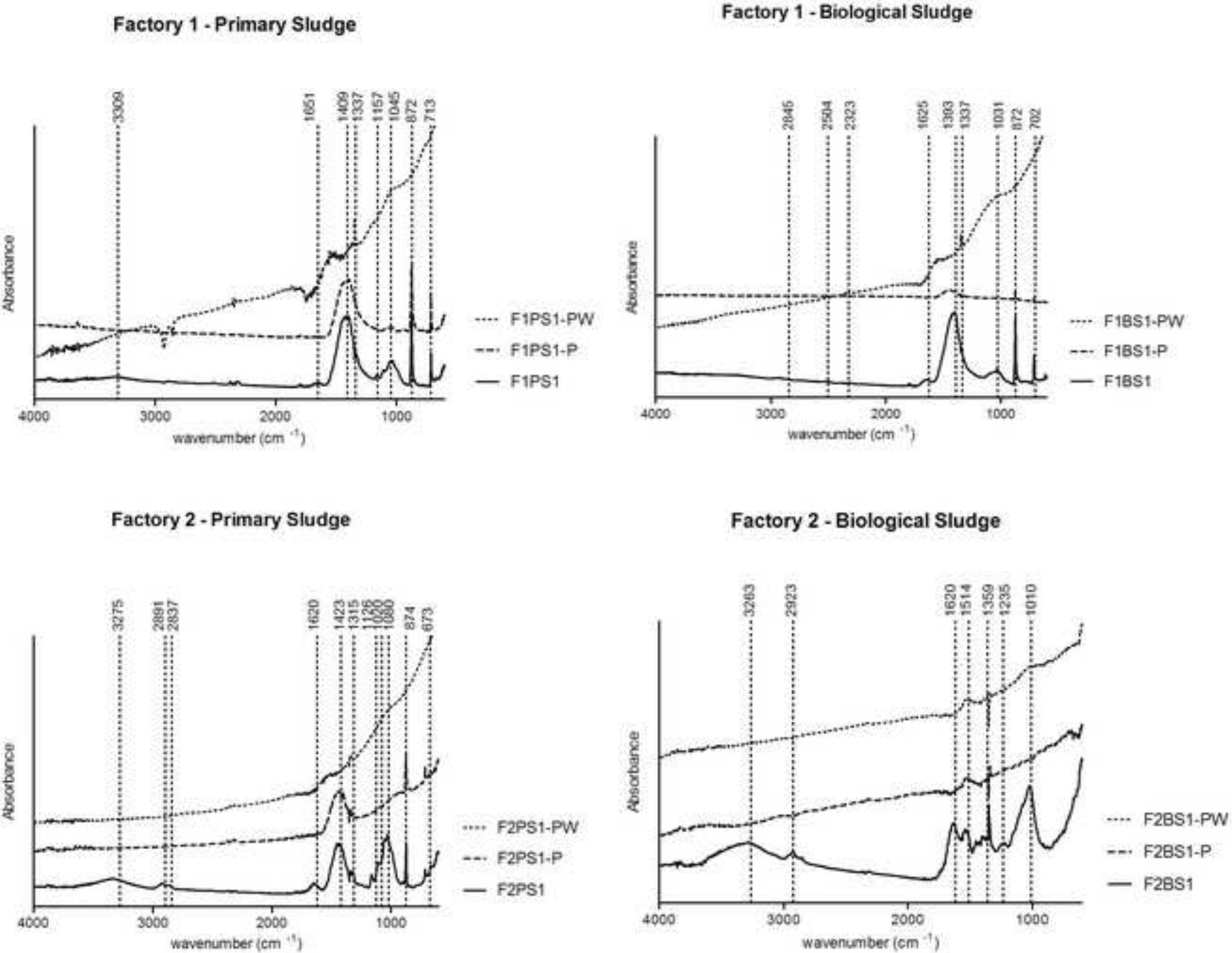


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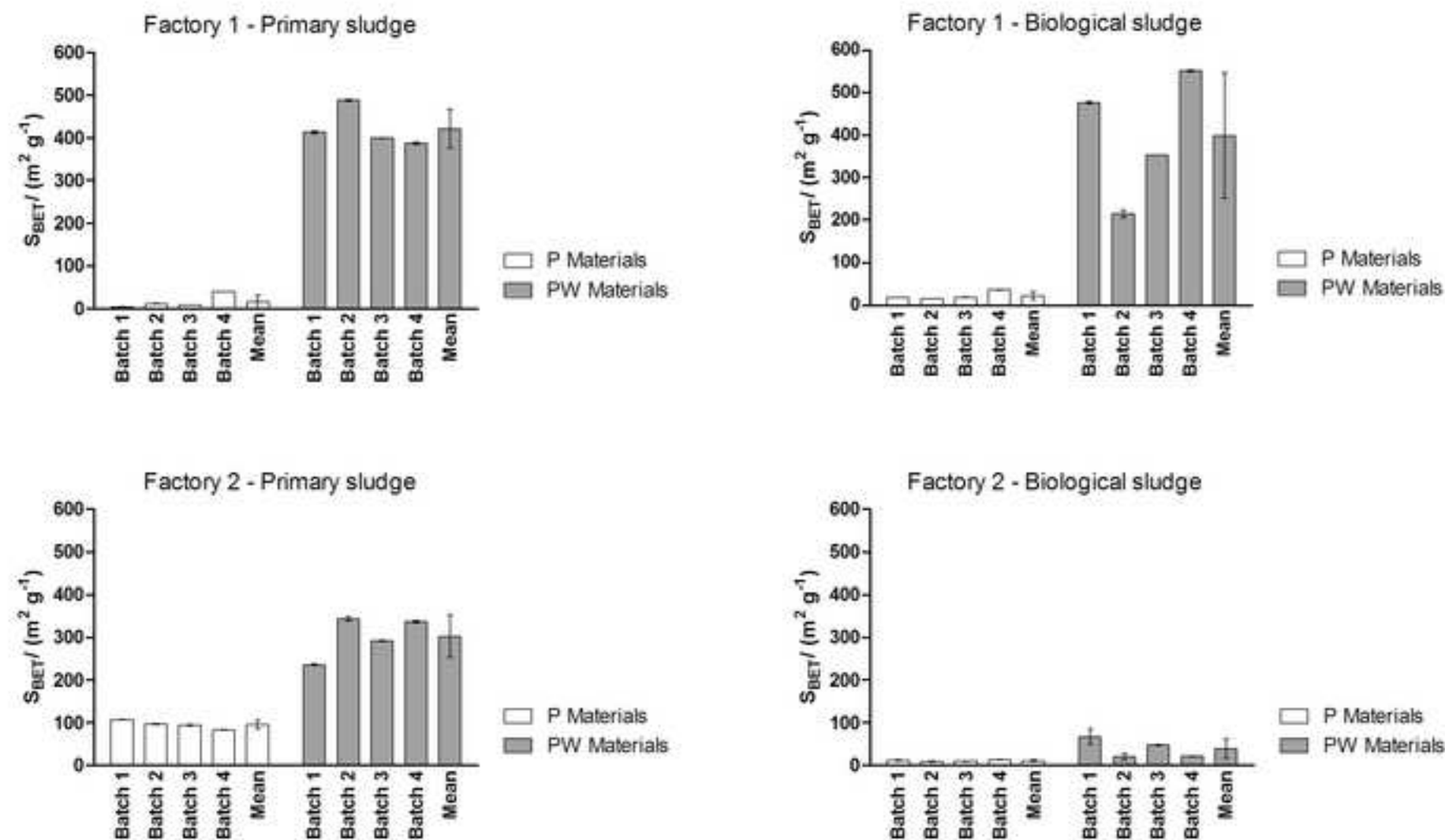
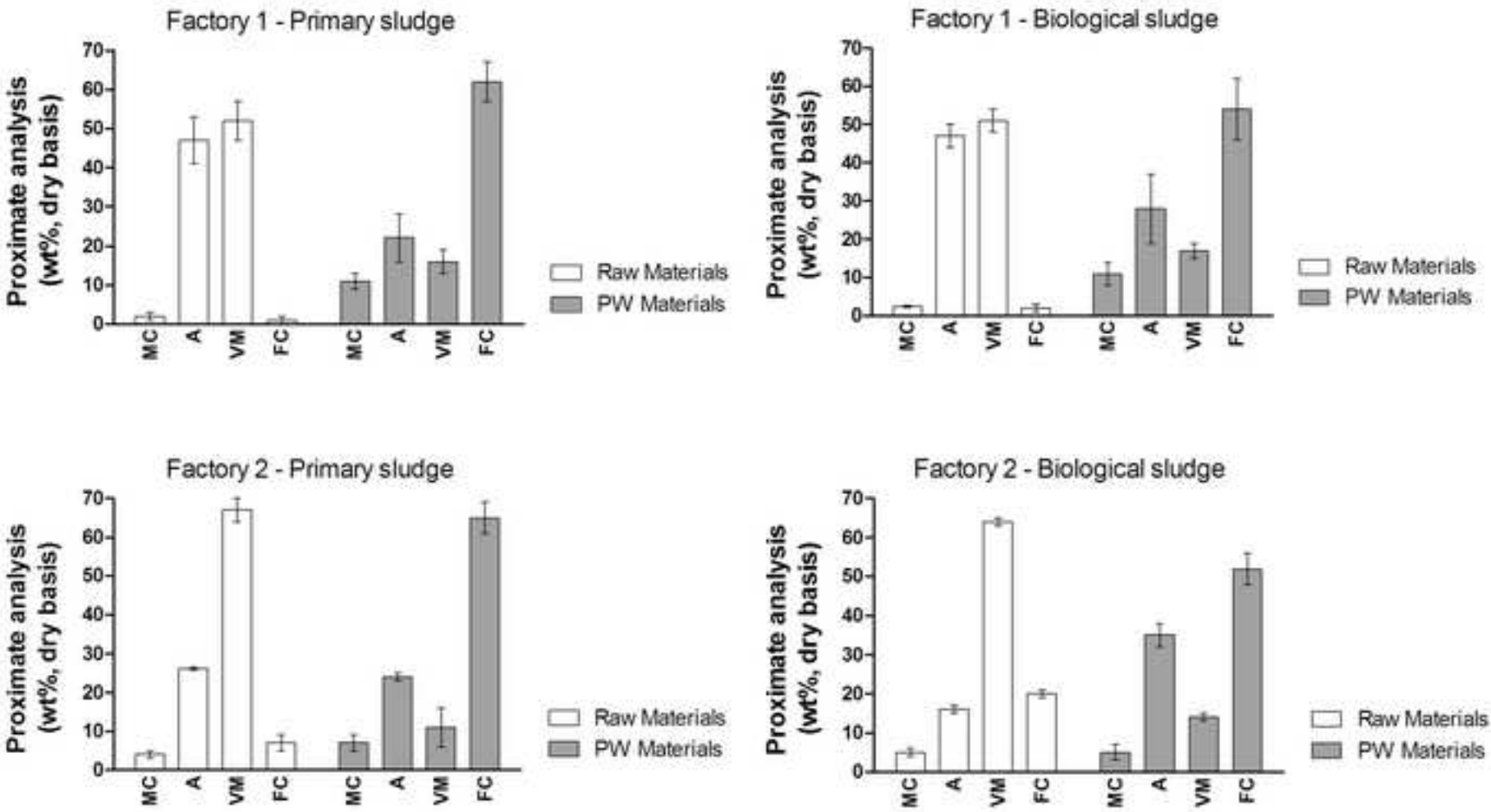




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